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CONSTRUCTION CERAMIC FROM TERRICONES IN THE KIZELOVSKII COAL FIELD

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It is shown that construction ceramic can be obtained from coal mine wastes, specifically, terricones in the Kizelovskii coal field in Permskii Krai. The use of oligopeptides increases the aggregative stability of disperse systems and terricones consisting of burnt and unburnt ceramic rocks with enhanced physical and mechanical properties.

Key words: terricones, transition elements, nanomodification, slip, plastic molding, semidry pressing, properties.

The need to eliminate terricones — wastes from exhausted coal mines — remains one of the most acute problems. Previous attempts at reclamation did produce the expected result. To improve the environment, specifically, in the Kizelovskii coal field (KCF), attempts are being made to salvage these wastes. One variant under consideration that could help solve the problem is to organize the production of ceramic brick.

On the basis of an analysis of previous research a hypothesis was developed concerning processes occurring in silicates, aluminum silicates and mixed sulfate-silicate disperse systems in the presence of oligopeptides [1]. It is based on an analysis of the similarity between the conditions of lithogenesis of naturally occurring mineral formations (rocks) and the technological characteristics of the processes used in the production of building materials. The essence of this hypothesis consists of the following.

Oligopeptides promote the dispersion of the disperse systems enumerated above. These systems acquire high aggregative stability via the oligopeptides. Owing to the absence of structuring the most disperse part of the system possesses the properties of gels. Under the influence of internal or external factors a gel transforms into a crystalline state. Possible external factors are an increase of the temperature and pressure and the action of physical fields. Impurities consisting of 3d and 5d transition elements, which are other initiators of crystallization, are possible internal factors [2]. This state of the system is nanostructural. Larger particles present in the system are bounded by a nanostructured shell (interlayer). At temperatures in the range 0 – 200°C the system can also contain water. At high temperatures, resulting in the removal of water and the formation of melt, it is possible to initiate, for example, by means of rapid cooling, the formation of a glass phase from gel that is capable of forming a sital in the presence of crystallization initiators and in the appropriate temperature-time regime. Both forms of the process represent a nanomodification of the material. The organic component of the system at high temperatures plays the role of a template, which from the technological point of view is an analog of a consumable additive and forms additional porosity. The technological characteristics of nanomodification depend on the particular phase and the chemical and disperse compositions of the initial system. The most suitable objects for using the nanomodification technology are construction mixtures that include technogenic materials (sludges, pitches, wastes and slags, which, as a rule, contain different kinds of initiators of crystallization of gels, hydrogels and glasses as well as highly disperse fractions of solid particles and, in a number of cases, surface-active organic impurities [3].

We have investigated on the basis of this hypothesis the effect of a protein foaming agent on the structure and properties of different kinds of construction ceramics. One objective of this investigation was to use Kizelovskii terricones as a source of crystallization initiators and simultaneously as a source of clayey components.

It should be noted that as a result of the unsuccessful attempts at the reclamation of terricones the burnt and unburnt rocks from the KCF turned out to be mixed with one another.

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TABLE 1. Optimal Batch Compositions used in Experiments

Ceramic type	Component content of batch, wt.%					
	Terricone mixture	Clay	CSOP	Cullet	Micro-cellulose	Water
Cellular	32.0	21.0	6.5	0	3.5	39.0
Plastic molding	50.0	18.0	5.0	7.5	0	19.5
Semidry molding	88.0	6.0	2.0	0	0	4.0

At this point it is impossible to separate them. For this reason, in reality, mixtures of both types of waste rocks were used in our experiments.

As previously determined, when such mixtures are used as a component of batch for ceramic they must be comminuted to full passage through a No. 0.63 sieve. Aside from mixtures of comminuted terricones the batch used for different types of ceramic contained clay, a colloidal solution of oligopeptides (in what follows designated by CSOP), finely comminuted cullet additives and microcellulose with different ratios of these components (Table 1). Here the types of construction ceramic are cellular ceramic and ceramic obtained by plastic and semidry molding.

Clay from the Fokinskoe deposit in Permskii Krai was used as the clay component. The composition of the clay was that of montmorillonite. The clay has coarsely disperse structure.

CSOP is a very effective foaming agent comprised of 30% oligopeptides and 70% water. The foaming ratio of the foam obtained from CSOP is at least 15 and the lifetime is 24 h. To obtain a cellular ceramic the CSOP was used to foam slip. Microcellulose was used as a thickener in the molding slip for cellular ceramic.

To increase the amount of melt in the process of firing plastic-molded ceramic samples the cullet consists of container glass and wastes from building fenestration.

The chemical composition of the terricones is indicated in Table 2.

The chemical compositions of the Fokinskoe clay and cullet are presented in Table 3.

Microcellulose is a waste from paper production.

Different methods were used to mold samples from the compositions presented in Table 1.

Thus, $4 \times 4 \times 16$ cm sample bars were molded from foamed slip by casting in a mold. To ensure that samples with this mass dried uniformly the molds were fabricated from paper-production wastes (piles). The latter comprise a mixture of unbleached cellulose and lignin and manifest binding properties. Owing to the high water absorption of and high moisture emission from a pile the sample cast in such a mold dries uniformly and does not deform in the process. The drying was conducted for 24 h at 80°C without removing the samples from the mold. Such samples were also fired directly in the mold, which burned up during firing.

The samples were fabricated from the plastic molding body in metal molds in the form of standard $4 \times 4 \times 16$ cm bars. Next, the samples were dried at room temperature in 6 h, after which they were removed from the molds and additionally dried for 12 h at 80°C.

The samples obtained by semidry molding comprised 5 cm high and 5 cm in diameter cylinders. They were obtained in compression molds under pressure 40 MPa. They were not dried prior to firing.

Different temperature-time regimes were used to fire the samples depending on the molding method (Table 4).

TABLE 2. Chemical Composition of Terricones

Batch No.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	S
1A	50.85	1.277	17.16	5.31	0.009	0.11	0.38	0.33	2.35	0.092	1.06
2A	51.04	1.449	21.75	14.16	0.019	0.00	1.60	0.45	2.25	0.114	1.96
3A	30.05	1.152	15.18	4.56	0.007	0.00	0.19	0.21	2.55	0.056	1.46
4A	45.22	1.295	17.11	9.65	0.007	0.11	0.16	0.23	2.43	0.076	1.10
1B	47.48	1.032	14.78	5.99	0.007	0.02	0.16	0.28	1.88	0.093	1.22
2B	52.99	1.383	19.88	14.31	0.020	0.00	1.92	0.31	2.07	0.105	1.87
3B	45.15	1.130	15.29	4.61	0.007	0.09	0.14	0.21	2.20	0.096	0.99
4B	58.67	1.192	16.57	8.34	0.013	0.24	0.13	0.22	2.29	0.095	0.82

TABLE 3. Chemical Composition of the Fokinskoe Clay and Cullet

Material	Content, wt.%										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	MnO	K_2O	Na_2O	SO_3	P_2O_5	other
Clay	62.20	12.52	5.12	4.95	2.07	0.68	1.80	2.21	2.11	0.04	0.30	6.00
Cullet	75.00	2.00	–	3.00	4.00	–	–	1.00	15.00	–	–	–

TABLE 4. Firing and Drying Regimes

Molding method	Drying		Firing			Cooling time, h
			Temperature rise	Isothermal soaking		
	Time, h	Temperature,°C	Time, h	Time, h	Temperature, °C	
Casting	24	80	6	8	1050	8
Plastic	12	80	4	8	950	6
Semidry	–	–	2	8	1050	6

The samples were subjected to tests for strength in compression and bending, and the water absorption, water resistance and frost resistance were determined. The cylindrical samples were tested by compression along the diameter.

The water resistance K_{dim} was determined at the ratio of the strength in compression of water saturated samples to the strength of dry samples.

The test results are presented in Table 5 for the optimal recipe.

These investigations have shown that the terricones can be used as the main component of ceramic bodies with any of the molding methods checked to obtain construction ceramic with high physical and mechanical properties.

It should be noted that the possibility of using terricones for the production of construction ceramic does not completely solve the problem of eliminating wastes in the near future. For this reason, in addition to using terricones from the production of construction ceramics, the search for other effective avenues should continue.

TABLE 5. Physical and Mechanical Properties of the Samples

Index	Molding method		
	Casting	Plastic molding	Semidry molding
Density, kg/cm^3	670	1331	1210
Strength, MPa:			
in compression	7.78	7.78	17.9
in bending	1.80	7.40	8.2
Water absorption, %	12.6	9.1	9.3
Water resistance, K_{dim}	0.72	0.87	0.92
Frost resistance, cycles	35	75	100
Thermal conductivity, W/(m · K)	0.239	0.64	No data

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